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Changes in the Polyunsaturated Fatty Acid Content of Potato Tubers During Growth, Maturation and Storage

SUMMARY—Kennebec and Red Pontiac potatoes were analyzed for fatty acids at intervals during growth and maturation of the tubers and subsequent storage at 4°C. During storage linoleic and linolenic were almost the only polyunsaturated acids present, but during growth and maturation considerable amounts of unidentified polyunsaturated acids were found. The percentage of polyunsaturated acids in the dry weight of tuber decreased to a low value near harvest time and remained near this value throughout the 6.3-month storage period, except that the value in Pontiacs stored 19 days was somewhat high. The percent of polyunsaturates in the total fatty acid fraction also dropped to a low value during growth and maturation but increased somewhat during storage. For this reason it may be better, when practicable, to make dehydrated products from freshly-harvested rather than from stored potatoes.

Potato dice contained as much polyunsaturated acid as the tubers they were made from; potato flakes contained somewhat less. In both products the degree of unsaturation of the fatty acid fraction was the same as for the tubers. No off-flavors were noticed when samples were reconstituted. Apparently little or no oxidation took place during the processing.

INTRODUCTION

THE QUANTITY OF LIPIDS in the white potato may be too small to be of nutritional significance. Various authors report values of 0.02 to 0.2 for the percentage of fat on a wet basis, as quoted by Lampitt *et al.* (1940). Völksen (1950) isolated and characterized linoleic and linolenic acids from potato fat but gave no quantitative data. Using spectrophotometric methods, Highlands *et al.* (1954) found 41% linoleic acid and 28% linolenic acid in the fat of Katahdin potatoes. Buttery *et al.* (1961) isolated linoleic and linolenic acids from Russet Burbank potatoes by use of gas chromatography and identified them by their infrared spectra; they reported 53% linoleic acid and 20% linolenic acid.

Because of the highly unsaturated nature of the fatty acids, the small quantity present is responsible for at least part of the oxidative off-flavor formed during the storage of dehydrated potato products. Burton (1949), Hendel *et al.* (1951), and Highlands *et al.* (1954) presented evidence indicating that certain off-flavors in dehydrated potato products are the result of unsaturated fatty acid oxidation. Buttery *et al.* (1961) demonstrated that during the storage of canned potato granules there is a correlation between the decrease in the unsaturation of the fatty acids, the decrease in the oxygen content of the head space, and the increase in off-flavor.

If there is a change in the concentration of polyunsaturated acids in potatoes during maturation or subsequent storage of the tubers, it may be possible to select a time for processing which will favor a reduced tendency toward the development of oxidative rancidity in dehydrated products.

Hilditch (1951) reviewed work showing a notable increase in unsaturation in many oil seeds during the final stage of ripening. For potatoes, little has been published on this subject. Mondy *et al.* (1963) analyzed potatoes stored for 2 to 16 weeks at 4°C. For Red Pontiacs, they found that the mole percentage of linoleic acid decreased from 51 to 7, but the corresponding values for linolenic increased from 16 to 37. However, for the Ontario variety, linoleic remained constant at 28%, and linolenic showed a slight decrease from 37% to 32%. In both varieties, total crude lipids decreased slightly. Cotrufo *et al.* (1964) reported a small increase in total fatty acids (averaged over nine varieties) during two months of storage at 22°C followed by a small decline in subsequent months.

The present study was made to follow changes in the polyunsaturated fatty acid concentrations which occur during growth, maturation, and storage of the tuber and to determine to what extent these acids were oxidized during processing.

EXPERIMENTAL

SAMPLES OF KENNEBEC AND RED PONTIAC potatoes grown in the Red River Valley were dug at intervals during growth and maturation and shipped to this Laboratory by Air Express. Ten pounds of each variety were sent in each of the first four shipments, 25 pounds of each in the fifth shipment. The first shipment, dug August 3, 1965, contained Kennebecs ranging in length from 2.5 to 7.5 cm and Red Pontiacs ranging in length from 3.5 to 7.0 cm. The fourth shipment consisted of potatoes dug on September 15—two days after the vines were sprayed with herbicide. Upon harvest (September 24), samples of the tubers were taken for the fifth shipment; the rest were cured for two weeks at 18°C and then put in storage at 4°C. Samples weighing 25 pounds were subsequently taken at various storage intervals and shipped to this Laboratory.

Upon receipt of the shipments, three representative samples of each variety were obtained by arranging the potatoes in order of size and selecting equal numbers of each size. Although the fat is more concentrated in potato peels than in the rest of the tuber (Völksen, 1950), most of the skin was removed by peeling for 20 sec in an abrasive peeler (Toledo Vegetable Peeler, Model A1-15) to simulate more nearly conditions in the potato processing industries. After this, stem material, buds and

sprouts, deep eyes and bad spots were removed. The potatoes were then rinsed, dried roughly, and French-fry sliced into strips about 6 mm thick. After the strips were mixed, 350-g samples were packed loosely into 125 mm diameter crystallizing dishes. These were placed in polyethylene bags and stored at −20°C until analyzed.

Potato flakes and dice were made by the Red River Valley Potato Processing Laboratory at intervals during storage of the tubers. Flakes were made by the potato flake process developed by Sullivan *et al.* (1961); dice were prepared by cooking diced potatoes and drying the dice in a forced-draft tray dryer. Upon receipt at this Laboratory, the processed products were removed from their bags, sealed in cans under nitrogen, and stored at −20°C.

Freeze-drying

Duplicate samples of the potato strips (the third sample was kept as a reserve) were transferred to stainless-steel screen baskets a little larger in diameter than the crystallizing dishes and freeze-dried on heated metal trays thermostatically controlled at 27°C (Lucite Tray Dryer L-100, Associated Testing Laboratories, Inc.). To follow the course of the drying, small metal thermometers were placed horizontally on the trays. A layer of Wood's metal was melted over the thermometer stems to hold them in place and to insure good heat conduction. Sublimation kept the shelf temperatures low during the freeze-drying; when they had risen to 27°C for a few hours, the drying was stopped.

Preparation of fatty acid methyl esters

The dried potatoes were ground in an Intermediate Model Wiley Mill with a 40-mesh screen. The ground material was mixed in a jar after the head space was filled with nitrogen, and duplicate 1 g samples were taken for determining solids by oven-drying at 110°C.

The potato lipids were saponified and the fatty acids extracted by a modification of the method used by Buttery *et al.* (1961) for potato granules. Sixty-g samples were mixed with a solution of 28.0 g KOH (assay 86%) in 350 ml of 90% ethanol. At this point, approximately 18 mg of methyl nonadecanoate or 30 mg of methyl behenate, weighed accurately on a microbalance, was added as a standard. The mixture was allowed to stand four days at room temperature and then filtered. The filtrate was concentrated in a rotary evaporator with bath temperatures below 38°C. After extraction of the unsaponifiables, the mixture was acidified to pH 2.0 with concentrated HCl (pH meter) to obtain the free acids.

Methyl esters were prepared by refluxing for 75 min a mixture of the acids in 5 ml of hexane with 70 ml of 5% H_2SO_4 (w/v) in dry methanol containing a crystal of hydroquinone. The reaction mixture was cooled and 30 ml of water was added. The mixture was then extracted with hexane and the resulting extract was washed with water and dried overnight with 4:1 anhydrous Na_2SO_4-$NaHCO_3$. It was then concentrated to about 5 ml under a nitrogen jet, passed through a 1.3 cm long 1.0 cm diameter column of Florisil, and concentrated further to about ¼ ml in a sample tube which had been drawn to a point.

Gas chromatography

Samples were analyzed on an F & M Model 810 Chromatograph with a thermal conductivity detector. The columns used were 8-ft by ¼-in. stainless steel tubing packed with 10% diethylene glycol succinate (Applied Science Laboratories, Pretested Grade) on 70–80 mesh Gas-Chrom RZ. Runs were made isothermally at 218°C with a helium flow of 60 ml/min. An Infotronics Model CRS-11HS digital integrator, connected directly to the output of the detector cell, was used to measure relative peak areas.

Methyl nonadecanoate was used as standard for the analysis of the first four potato shipments. However, by the fifth shipment it was apparent that only a slight deterioration of the chromatographic column was resulting in poor resolution of the nonadecanoate and linolenate peaks. For this reason both nonadecanoate and behenate were used for analysis of the fifth shipment, and only behenate was used in subsequent analyses, because its elution time was sufficiently different from that of all the potato acids. No difference was found between results based on the two standards.

RESULTS AND DISCUSSION

Two types of determination have a bearing on this study—the percent of the total potato solids represented by the polyunsaturated acids and the percent of the total fatty acid fraction represented by the polyunsaturated acids. The concentration of these acids in the total solids should affect the amount of oxidation products that accumulate in dehydrated potatoes. This value was calculated by comparing peak areas with the peak area produced by a known quantity of standard. The concentration of polyunsaturates in the total fatty acids, which was calculated from relative peak areas alone, should affect the rate at which the oxidation products form (Bolland, 1948; Buttery *et al.*, 1961).

To calibrate the gas chromatographic method, weighed amounts of methyl behenate and a standard mixture of methyl palmitate, stearate, oleate, linoleate and linolenate (Applied Science Laboratories, Inc. mixture K-108) were made up to volume in separate flasks. The two solutions were mixed in varying proportions and samples were run on the gas chromatograph. Ratios of the weight of each ester to that of the methyl behenate ranged from 0.2 to 3.6. Sample sizes were chosen to give a methyl behenate peak area similar to that which was maintained in analyzing the potato samples. Plots of weight ratios of each ester to behenate versus the corresponding peak area ratios showed a linear relationship. Although detector response was somewhat lower for late-appearing peaks, correction factors were not used because errors were too small to affect conclusions concerning change with tuber maturity or storage time.

The over-all precision of the analytical method was estimated for linoleic and linolenic acids by calculating the coefficient of variation (the Standard Error for duplicate determinations × 100 divided by the mean). This value differed somewhat depending on whether the seven larger values for each ester (seven including results for both varieties, Tables 1 and 2) or the 10 smaller values

Table 1. Changes in acid concentrations in Red Pontiac potatoes.[1]

	Maturation					Storage			
Date	8/3/65	8/16	8/30	9/15	9/24[2]	10/13	11/23	1/24/66	3/30
Palmitic	.27	.29	.34	.12	.12	.19	.094	.098	.095
Stearic	.026	.029	.026	.017	.020	.042	.015	.016	.016
Oleic	.010	.012	.015	.004	.005	.009	.003	.003	.009
Linoleic	.46	.64	.50	.094	.14	.29	.17	.16	.14
Linolenic	.24	.33	.29	.044	.062	.14	.074	.088	.10
Unidentified[3]	.14	.051	.33	.059	.026	.002	.001	0	0
Total acids	1.21	1.42	1.63	.35	.38	.72	.36	.37	.37
Percent unsaturates[4]	73	75	74	58	60	64	68	67	66

[1] Average of duplicate determinations reported as percent methyl ester on potato dry matter.
[2] Date of harvest; potatoes were planted on 5/28.
[3] Includes only one peak; other unidentified peaks very small.
[4] Percent polyunsaturated esters based on total fatty acid esters.

Table 2. Changes in acid concentrations in Kennebec potatoes.[1]

	Maturation				Storage			
Date	8/3/65	8/16	8/30	9/15[2]	10/13	11/22	1/24/66	3/29
Palmitic	.19	.31	.22	.11	.12	.084	.079	.078
Stearic	.024	.029	.023	.020	.022	.017	.015	.017
Oleic	.007	.014	.009	.006	.005	.003	.003	.004
Linoleic	.47	.48	.36	.18	.17	.16	.17	.14
Linolenic	.16	.19	.14	.064	.054	.071	.076	.074
Unidentified[3]	....	.32	.15	.027	.026	.004	0	0
Total acids	.88	1.48	.95	.42	.41	.35	.35	.32
Percent unsaturates[4]	73	73	72	66	62	68	71	68

[1] Average of duplicate determinations reported as percent methyl ester on potato dry matter.
[2] Vines killed on 9/13; potatoes were planted on 5/28, harvested on 9/24.
[3] Includes only one peak; other unidentified peaks very small.
[4] Percent polyunsaturated esters based on total fatty acid esters.

were used in its calculation. The coefficients for the linoleate determination were 11.3% for the large values and 8.1% for the small; the corresponding coefficients for the linolenate determination were 13.2% and 12.9%.

Changes in the concentrations of linoleic and linolenic acids in the tubers both followed the same trend. Fig. 1 shows changes in the sum of the two and also changes in concentration of the largest unidentified peak. Mass spectroscopy indicated the latter to be a mixture with molecular weights corresponding to those of long-chain polyunsaturated acids. Although not fully identified, the mixture does not affect the overall conclusions since its concentration mainly follows the same trend as that of the known polyunsaturated acids. Other unidentified peaks were too small to be of consequence.

Fig. 1 shows that in immature tubers the percent of polyunsaturates on the dry weight of potatoes is very high, falls to a low point near harvest time, and then remains fairly constant during storage. Exceptional is the high value in Pontiacs which had been stored 19 days. Results calculated on a fresh-weight basis would be similar for the stored potatoes since the concentration of solids does not change during storage. However, since immature tubers are low in solids (Murphy *et al.*, 1959), fresh-basis values would be lower for this period.

In Fig. 2 the percent of polyunsaturated acids in the total fatty acids is shown. As in the case of the percent based on total solids, this value for the Pontiacs starts out high in the immature potatoes and soon falls to a low point near harvest time. For the Kennebecs the trend is similar, but no data were obtained on the freshly-harvested potatoes; the low point shown is for tubers stored 19 days. In both varieties the fatty acid fraction of stored potatoes is

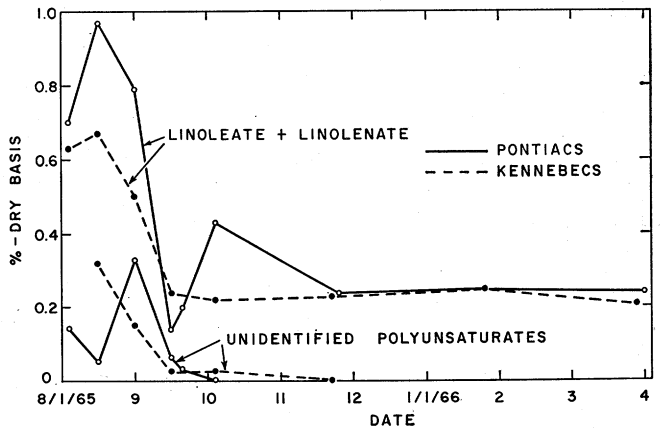

Fig. 1. Variation of the dry weight percentage of polyunsaturated fatty acids in tubers with growth, maturation, and storage time. The potatoes were harvested on 9/24/65. Results are plotted as percent methyl ester on dry weight of tuber.

Table 3. Acid concentrations in flakes prepared from potatoes stored for various periods.[1]

Date of preparation	Red Pontiacs				Kennebecs			
	10/8/65	11/16	1/20/66	3/29	10/8/65	11/16	1/20/66	3/29
Palmitic	.....[2]	.....	.053	.077	.....[2]	.....	.047	.054
Stearic	.....	.....	.011	.013	.....	.....	.011	.011
Oleic	.....	.....	.002	.002	.....	.....	.002	.001
Linoleic	.15	.19	.10	.13	.14	.13	.11	.11
Linolenic	.051	.065	.039	.074	.040	.044	.039	.051
Total acids	.....	.....	.21	.30	.....	.....	.21	.23
Percent unsaturates[3]	.....	.....	66	68	.....	.....	70	70

[1] Average of duplicate determinations reported as percent methyl ester on potato dry matter.
[2] The first two samples of flakes (of each variety) had been treated with an additive.
[3] Percent polyunsaturated esters based on total fatty acid esters.

more unsaturated than that of potatoes analyzed near harvest time.

From both Figures it appears that nothing can be gained by processing somewhat immature potatoes but, from the standpoint of the degree of unsaturation of the fatty acid fraction, it is better to process freshly-harvested potatoes than stored potatoes. However, this is not often practical since most dehydration plants must use stored potatoes.

The concentrations of palmitic, stearic, and oleic acids in the potato solids, and that of the total acids (Tables 1 and 2), follow the same trends noted for the polyunsaturated acids during the growth and maturation of the tuber.

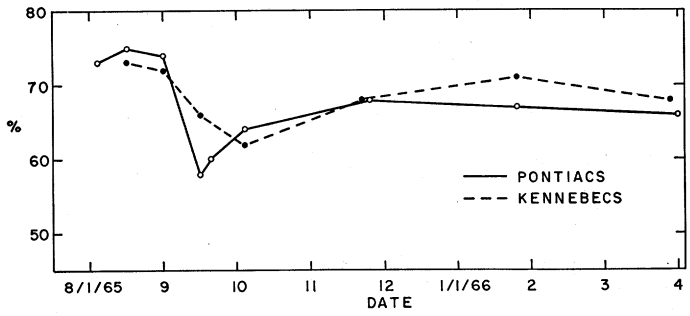

Fig. 2. Variation of relative concentrations of polyunsaturated acids in the fatty acid fraction during growth, maturation, and storage of tubers. The potatoes were harvested on 9/24/65. Results are plotted as percent methyl ester on total weight of fatty acid esters.

Table 4. Acid concentrations in dice prepared from potatoes stored for various periods.[1]

Date of preparation	Red Pontiacs			Kennebecs		
	11/24/65	1/20/66	3/28	11/24/65	1/20/66	3/28
Palmitic	.069	.090	.093	.089	.074	.073
Stearic	.014	.013	.014	.014	.015	.015
Oleic	.004	.004	.004	.003	.004	.003
Linoleic	.16	.16	.17	.17	.16	.14
Linolenic	.053	.074	.10	.061	.067	.071
Total acids	.31	.35	.39	.35	.32	.31
Percent unsaturates[2]	70	68	70	68	70	69

[1] Average of duplicate determinations reported as percent methyl ester on dry matter.
[2] Percent polyunsaturated esters based on total fatty acid esters.

As in the case of the latter acids, changes during growth and maturation were much more pronounced than during storage.

Fatty acid composition of the potato flakes and dice is shown in Tables 3 and 4. The dice contain about the same amount of unsaturates as the tubers from which they were made; the flakes contain somewhat less. In both products the degree of unsaturation of the fatty acid fraction is the same as for the tubers. No off-flavors were noticed when samples of the flakes and dice were reconstituted. Apparently little or no oxidation took place during the processing.

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Mention of company or product names does not imply recommendation of the products by the U. S. Department of Agriculture over others that may be suitable.

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